E. R. D. E. 25/R/49

SECRET - DISCREET

MINISTRY OF SUPPLY

EXPLOSIVES RESEARCH & DEVELOPMENT ESTABLISHMENT

REPORT No. 25/R/49

20071109138

INV 90

An Assessment of Hydrazine, Hydrazine Hydrate and
Liquid Ammonia as fuels for Rocket Propulsion

K. A. Cooper & L. A. Wiseman

REGRADED _Conf_ BY AUTHORITY OF
R + D Abstracts vol 11,
DATED. _1958_ BY _244_

Waltham Abbey,
Essex.

August,
1949

E.R.D.E. 25/R/49.

~~CONFIDENTIAL~~

X.R. 460/23.

UNCLASSIFIED

MINISTRY OF SUPPLY.

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT.

E.R.D.E. REPORT NO. 25/R/49.

An Assessment of Hydrazine, Hydrazine Hydrate and
Liquid Ammonia as fuels for Rocket Propulsion.

by

K.A. Cooper & L.A. Wiseman.

This Report contains information of overseas origin.

Submitted by :- C.H. Johnson.
C.H. Johnson,
S.P.R.II.

Approved by :-
H.J. Poole
C.S.,E.R.D.E.

WALTHAM ABBEY,
ESSEX.

Best Available Copy

UNCLASSIFIED

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

DISTRIBUTION.

EXTERNAL.

T.P.A.3./T.I.B. (41)
B.J.S.M., thro' T.P.A.3., Dr. Masterman and
                                    Dr. Dodds.

Ministry of Supply.

Chief Scientist
C.S.(M)
C.I.
C.D.E.E. (2)
C.E.A.D. (2)
I.A. (Air) R.A.E., Farnborough.
C.S.A.R. (2)
D.Amm.P.
A.D.Amm.P(X) (Mr. Corbell)
D.E.R.D. (Dr. Hall)
D.M.X.R.D. (3)
D.R.A.E. (3) (including Dr.Parker & Dr.Murray)
D.G.W.R.D.
D.O.F.(X)
D.O.F.(F)
D.W.P.
D.W.R.(D)
P.D.S.R.(A)
P.D.S.R.(D)
Sec. O.B. (2)
A.D./G.W. (R. & D.)
R.A.E./R.P.D. (Westcott) (6) (including Mr.Baxter,
                            Dr. Merrington, Dr. Maxwell)
S.A.C., L.F.C. Committee (45)
Chairman S.A.C.
Chairman M.C.A.B.

War Office.

M.C. of S. Shrivenham (2)
S.A./A.C.

Air Ministry.

S.A./A.M.
D.D.O.R. (2)
D. of Weapons

Admiralty.

A.C.S.I.L.
D.A.E.R.
D.N.O.
D.U.W.
Supt., A.M.L. (3) (including Mr. Borrows & Dr. Hart)

/INTERNAL

INTERNAL.

C.S./E.R.D.E.
S.P.R.I.
S.P.R.II.
S.E.I.
S.C.E.
Dr. Cooper
Mr. Hill
Dr. Pryde
Mr. Verschoyle
Mr. Wiseman
Tech. Reg. (2)
Library   (12)

Further copies of this report can be obtained from
Chief Superintendent, Explosives Research & Development
Establishment, Waltham Abbey, Essex.

C.S./E.R.D.E.
S.P.R.I.
S.P.R.II.
S.E.I.
S.C.E.
Dr. Cooper
Mr. Hill
Dr. Pryde
Mr. Verschoyle
Mr. Wiseman
Tech. Reg. (2)
Library   (12)

CONTENTS.

Reference X.R. 460/23.

1. SUMMARY.

The use of the fuels liquid ammonia, hydrazine hydrate and anhydrous hydrazine in the field of rocket propulsion has been assessed. It is concluded that liquid ammonia is not promising except possibly in small motors where its high vapour pressure may not be too severe a disadvantage. More data on the system Hydrazine/water, in which the concentration of water is less than in hydrazine hydrate, are desirable, and other methods of lowering the freezing point of anhydrous hydrazine should be investigated. If chlorine trifluoride is developed as an oxidant it will probably be essential to have hydrazine or hydrazine/water as the fuel.

2. INTRODUCTION.

A large amount of attention has been paid to methods of obtaining higher performances than are possible with the normal oxidants and fuels such as hydrocarbons or alcohols. Thus with HNO_3 or 85% H.T.P. and kerosine at a combustion pressure of 20 ats. a Specific Impulse of about 220 secs. is theoretically possible and, with liquid oxygen and kerosine, one of about 240 secs. A higher performance can be obtained,

a) by increasing the combustion pressure

b) by using oxidants such as liquid fluorine or chlorine trifluoride

c) by using fuels such as hydrazine, certain hydrides of light elements such as B_2H_6, and liquid hydrogen.

Methods b) and c) are not independent since the use of the fluorine group of oxidants probably requires fuels which contain no carbon in order to avoid the formation of the very stable CF_4. We have therefore critically examined the merits of hydrazine, hydrazine hydrate and liquid ammonia as fuels both with the three normal oxidants and with chlorine trifluoride, a typical representative of the fluorine group.

3. AVAILABILITY & PRICE.

Ammonia.

Although the annual production in Great Britain is of the order of 400,000 tons per annum, it is insufficient to meet all requirements and any substantial new demand would probably require new plant. The current market price is about £27 per ton in bulk.

Hydrazine Hydrate.

There is at present no large-scale production in Great Britain, but it has recently been reported (1) that the firm of Chemicals and Biologicals Ltd., has been running a pilot plant for more than a year; and this firm claims to have made significant improvements in the Raschig process.

In Germany, by the end of World War II, there were two main factories producing hydrazine hydrate. The first, at Leverkusen, contained a pilot plant with a rated capacity of 50

/tons

- 1 -

tons per month.   The second, at Gersthofen, had been planned
to contain four separate 100 ton per month units.   Of these,
however, only one was built and working (and owing to supply
difficulties it never exceeded 50 tons per month production);
a second was very nearly complete.   The Gersthofen plant has
recently been brought to Great Britain.   It is understood
that a part of it, capable of 30-35 tons per month production,
is to be transferred to Chemicals and Biologicals Ltd., and
that a similar portion imay be set up at R.O.F. Bridgwater,
the rest remaining in store.   Hence a total production of 60
tons per month should eventually be available in Britain, with
a reserve capacity which would bring the total to 100-200 tons
per month.

Both the German plants used a modification of the Raschig
process, in which sodium hypochlorite interacts with ammonia
in aqueous solution according to the equations :-

$$NaOCl + NH_3 = NaOH + NH_2Cl \qquad (i)$$

$$NH_2Cl + NH_3 = HCl + N_2H_4 \qquad (ii)$$

$$2 NH_2Cl + N_2H_4 = 2 NH_4Cl + N_2 \qquad (iii)$$
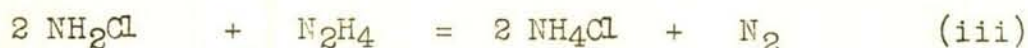
(iii) being a side-reaction which reduces the yield, and which
is suppressed to some extent by the addition of glue as an
anticatalyst.   In the German plants this reaction took place at
about 160°C. under 30 atmospheres pressure, the reaction time
being a matter of seconds.   The hydrazine hydrate, which was
formed in dilute solution, was concentrated and separated from
sodium chloride and ammonia in a series of evaporations and
rectifications;   the final product was of 80 to 95 per cent
strength as N_2H_6O.

The materials required for this process are ammonia and
electrolytic chlorine.   (The latter could be recovered, if
needed, from the sodium chloride produced, though at Gersthofen
this was not done.   A tenfold excess of ammonia was used,
with continuous recycling).   Besides the electrical energy
needed for production of chlorine, a large amount of steam was
consumed for heating purposes.   200-250 Kg. of steam (part of
it superheated) was used up for every kilogram of hydrazine
hydrate produced (2).

The price of hydrazine hydrate was R.M. 4 per Kg.   This
may be compared with R.M. 1.9 per Kg., the price of 80 per cent
H_2O_2.   If the ratio of costs under British conditions of manu-
facture is about the same as for German, this would correspond
to a price of 4s. per lb. for hydrazine hydrate made in Britain;
but this is a very rough estimate.

The Western Cartridge Co. in the U.S. is currently pro-
ducing hydrazine hydrate at a market price of 50 cents per pound.

A process which resembles the Raschig process to some extent
is the oxidation of urea with sodium hypochlorite in the presence
of excess alkali, the overall reaction being :-

$$CON_2H_4 + 2 NaOH + NaOClCl = Na_2CO_3 + NaCl + N_2H_4 + H_2O.$$
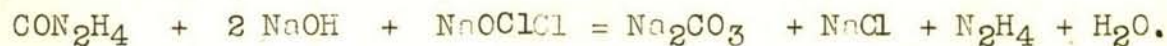
According to some authorities the urea and alkali simply
act as a source of ammonia, which then reacts exactly as in the

/Raschig

- 2 -

Raschig synthesis.   The urea process was worked in Germany towards the end of the war by I.G. Ludwigshafen in a plant of 15 tons per month capacity, to supplement the production in their high temperature ammonia-hypochlorite plant at Leverkusen.   It is also used by at least one American firm at the present day.

No alternative method of preparation of hydrazine hydrate is at present available in Britain.   Two possibilities should, however, be mentioned :-

(i)   Academic research work by Dr. Ross at McGill University, Canada, indicates that a process involving the inter-action of hydrocyanic acid, potassium bisulphite and nitrous acid would give good yields by a safe process. The economic practicability is, however, very doubtful, and there has been no development beyond the laboratory stage (3).

(ii)   If anhydrous hydrazine can be produced by any method which does not proceed via the hydrate (see below), then of course the hydrate, or a hydrazine-rich mixture, could be made simply by mixing with water.

There are a number of other processes by which hydrazine has been synthesised in the laboratory. These include, for instance, reduction of nitrous oxide, hyponitrites, or potassium nitrososulphite; decomposition of aminoguanidine; hydrolysis of bis-diazo acetic acid; and also a cyclic process due to Aston (et.al.) (6), in which methyl isopropyl ketone reacts with ethyl nitrite, and the resulting complex is reduced with formation of hydrazine and regeneration of the ketone.   None of these methods, however, has so far been shown to be commercially practicable.

It should be added that some 45 tons of hydrazine hydrate of German origin is in store in Britain in the charge of ..D. Amm. P. (X), Ministry of Supply.

Hydrazine.

There has as yet been little commercial manufacture of the anhydrous material.   The processes which are open to consideration at the moment are the following :-

(i)   Dehydration of hydrazine hydrate.

This may be carried out with caustic alkali, quick-lime or baryta.   The method is probably suitable for laboratory scale work, but for plant-scale work it has considerable disadvantages.   In the first place the process is long and cumbrous, in the second it is not yet certain that it can be operated under safe conditions.   These disadvantages should not be so formidable if only a partial dehydration were desired.   In this case the procedure might be facilitated by making use of a recent discovery of Audrieth and his collaborators (4), that above 60°C. certain mixtures of $N_2H_4.H_2O$ and NaOH separate into two liquid phases, the less dense of which contains

/most

- 3 -

most of the hydrazine and least of the alkali
(see Appendix II, Table VIId).

(ii) Ammonolysis of Hydrazine Sulphate.

Since the salt $N_2H_4.H_2SO_4$ is nearly insoluble in
water, it can easily be separated at an early stage
of the Raschig process.   It has been shewn, on a
laboratory scale, that hydrazine is obtained by re-
action of this salt either with gaseous ammonia at
$150^{\circ}C$. or with anhydrous liquid ammonia at low
temperatures;   in the latter case the solid reaction
product (an ammoniated ammonium sulphate) is insoluble
in the liquid NH_3.   A method is thus made available
which avoids not only the difficult dehydration of
hydrazine hydrate but also the rectification needed
to produce the pure hydrate.   The separation of
hydrazine and ammonia is easy, as they form no com-
pound and have widely different vapour pressures.

The process using liquid ammonia has been developed
to a pilot plant stage by the Mathieson Chemical
Corporation in America.   It is understood that 3,000
lbs. per month of hydrazine are being produced at 5
dollars per pound.

(iii) Synthesis from the elements or from ammonia.

Various authors have reported the formation of traces
of hydrazine when either ammonia gas, or a mixture of
nitrogen and hydrogen, is subjected to electrical dis-
charge or to the action of ultraviolet.   A review of
the literature, together with a statistical-mechanical
calculation of equilibrium constants of possible re-
actions, was made by A.G. Parts in 1945.   Parts con-
cluded that the yields from either process were likely
to be too small to be of practical use;   though the
oxidation of ammonia to hydrazine with either oxygen
or nitric oxide would be possible if selective catalysts
could be found.(5).   Parts' calculated equilibrium
constants for the synthesis $N_2 + 2H_2 \longrightarrow N_2H_4$ are
in quite good agreement with those recently published
by Scott and his collaborators.(32).   The value of Kp
is about 10^{-19} at $700^{\circ}C$. and about 10^{-15} at $1500^{\circ}C$.

Recently, however, the Batelle Memorial Institute
in the United States has claimed the discovery of a
process in which gaseous ammonia is passed through a
corona discharge;   a small quantity of hydrazine is
produced, which is separated by refrigeration;   the
ammonia is then recycled.   The yield of hydrazine is
said to be sufficient to justify some confidence in
the commercial practicability of the process.   It is,
however, at the moment in a very early stage of develop-
ment.   It is understood that the Batelle Memorial
Institute hope to have a small pilot plant in operation
by about the end of 1950, which should produce a few
pounds of hydrazine per day at a cost of 20 to 30 cents
per lb.

Research on the oxidation of ammonia to hydrazine
is also being carried out in America but so far no report
has been received of any process which offers commercial
prospects.

/4.

- 4 -

4.   PERFORMANCE.

        In this section the necessary data on Specific Impulse,
combustion temperature and physical properties, in so far
as they influence operational use and cooling of motors, will
be reviewed.   For comparison purposes the propellant system
HNO$_3$/n-decane, will be taken as the norm.
The necessary performance data for HNO$_3$ with the fuels n-decane
N$_2$H$_4$. H$_2$O, N$_2$H$_4$ and liq. NH$_3$ are given in Table I and in
Figs. I & III.   It is clear from these figures that anhydrous
hydrazine, N$_2$H$_4$, is superior to the other fuels, both on a
weight and on a volume basis.   In order to show that this
result is general, the performance figures for Chlorine Tri-
fluoride with N$_2$H$_4$, liq.NH$_3$ and N$_2$H$_4$.H$_2$O are given in Table II
and in Figures II and IV, and some figures for liquid oxygen
(Ref.7) are given in Table III.   In particular, the perform-
ance of the propellant, ClF$_3$/N$_2$H$_4$, on a volume basis, is
definitely better than that of any of the systems based on
liq.O$_2$ (Table III) or HNO$_3$.   We shall therefore discuss the
physical properties of hydrazine a little more fully.

Anhydrous Hydrazine.

        The first point to note is that the combustion temperatures
with this fuel and the oxidants liq.O$_2$ and HNO$_3$ are only 200-
400°C. below those with a hydrocarbon fuel and the optimum
performance of the propellant, ClF$_3$/N$_2$H$_4$, has a combustion
temperature of about 3500°K.   It will therefore be necessary
to cool motors using N$_2$H$_4$ as fuel if advantage is to be made of
its higher performance.   If the oxidant is HNO$_3$, the HNO$_3$
can be used as the regenerative coolant but, if the oxidant
is ClF$_3$, or even F$_2$, then it may not be possible to use the
fluorine-containing compound as a coolant owing to the very
high reactivity of these compounds.   Thus we must consider
the possibility of using anhydrous hydrazine as a coolant
when the combustion temperature is at least 2800°K and may be
3500°K.

        The thermal stability of hydrazine has not been exhaustively
investigated up to now but, in the absence of catalysts, it
seems to be reasonably stable at least up to 150°C (see section
6).   This means that anhydrous hydrazine is considerably more
stable than H.T.P. and H.T.P. has been successfully used for
the regenerative cooling of rocket motors.   Thus, the thermal
stability is sufficient to allow its use as a regenerative
coolant.   The critical pressure is high but this disadvantage
is not important because the vapour pressure is low and there-
fore, if thermal decomposition can be avoided, the formation
of bubbles in the cooling jacket will not occur at the feed
pressures normally used in rockets.   Some preliminary results
on the cooling of a rocket motor with 90% Hydrazine have been
reported (8) for a motor working with the propellant, H.T.P./
nitromethane.   The hydrazine was used for cooling just one
section of the combustion chamber, the combustion temperature
being about 2800°K. according to calculations of Stosick (9).
The total time in contact with a hot surface is smaller than
in the case of complete regenerative cooling and the heat trans-
fer is not so great as when the nozzle is also cooled.   However,
stable conditions in the coolant were obtained up to a measured
bulk temperature of about 190°C in the coolant.   When the bulk
temperature of the hydrazine reached 240°C., there was some
evidence of decomposition as shown by a sudden rise in temper-
ature.   It seems therefore that it would be possible to use

                                              /hydrazine

                            - 5 -

hydrazine as a regenerative coolant although it is clearly necessary to carry out calculations on the conditions for which it can be used, i.e. size of motor as a function of combustion temperature.

The main handicap to the use of hydrazine as an operational fuel is its high melting point. There are two obvious ways of lowering the melting point, firstly by adding Hydrazine Hydrate and secondly, by adding ammonia. These two diluents have one obvious advantage in that both lead to lower combustion temperatures. However, hydrazine hydrate is to be preferred because its density is much higher than that of ammonia, and its vapour pressure is much lower. Thus, on a volume basis and with ClF_3 as oxidant, the performance with the fuel, Hydrazine + Hydrazine Hydrate would lie between 320 and 360 and with the fuel, Hydrazine and Ammonia, between about 300 and 360 as compared with the figure 280 for the propellant HNO_3/n-decane.

Hydrazine Hydrate.

The performance of this fuel is lower than that of Ammonia with both HNO_3 and ClF_3 on a weight basis, but definitely better on a volume basis, thus $ClF_3 + N_2H_4.H_2O$ is better than $HNO_3 +$ n-decane and $HNO_3 + N_2H_4.H_2O$ is as good as $HNO_3 +$ n-decane. This fuel has a definite advantage over hydrazine and hydrocarbons as the combustion temperature is about 500°C. lower. The use of Hydrazine hydrate will probably be in lowering the combustion temperature of propulsive systems and in combination with anhydrous hydrazine.

Hydrazine hydrate was developed in Germany as a fuel, because it could be used as a self-igniting fuel with H.T.P. For this purpose, the hydrate (80-92 per cent) could be used, or a mixture with methyl alcohol and a little water ('C-stoff'). To these mixtures it was necessary to add a trace of a catalyst, to insure spontaneous ignition with 80 per cent H_2O_2. The usual catalyst was potassium cuprocyanide. C-stoff was used in the Me.163 fighter plane, and hydrazine hydrate was to be used as an igniter in the Walter Torpedoes, which were under development at the end of the war. The mixtures containing cuprocyanide were not entirely satisfactory, owing to a tendency for the copper to come out of solution when the liquid was stored in metal containers. Ignition delays, in bifuel systems using H.T.P. with either hydrazine hydrate or 'C-stoff', may be as long as 40-50 milliseconds at ordinary temperatures. A report from Massachusetts Institute of Technology (29) states that the use of potassium cuprocyanide and sodium nitroprusside. together will reduce the ignition delay, with 85 per cent. hydrazine hydrate and H.T.P., to 7 milliseconds at 100°C. and to 13 milliseconds at 0°C. The actual catalyst recipe was 0.20 grams Fe as sodium nitroprusside, 0.33 grams Cu as cuprous cyanide, and 0.24 grams K as potassium cyanide, per litre of hydrazine hydrate. Anhydrous hydrazine ignites spontaneously with H.T.P.; with catalysts, the delay can be reduced to about 3 ms.(35).
Ammonia.

The disadvantages of this fuel are its high-vapour pressure and low density. The high vapour pressure and the high critical pressure (111.5 ats.) mean that ammonia would be a bad coolant owing to the difficulty of avoiding gas formation in the boundary layer without very high rates of flow or high pressures. On the other hand, its availability and the low combustion temperature are attractive, but it is doubtful whether these are sufficient

/to

to compensate for its high vapour pressure, e.g. a stronger propellant tank would be required except in the case of small units, where gas pressure or expulsion charges would be used for feeding the propellant components, but in such units the low density would be a great disadvantage.

A possible solution would be the addition of substances to lower its vapour pressure and raise its density, Anhydrous Hydrazine is one such possibility but the vapour pressure data in Table VIII, Appendix 2, shows that it is not very effective.   The alkali and alkaline earth metals are very soluble in liquid ammonia.   The only one which would not lower the performance appreciably is Lithium, although it would raise the combustion temperature.   Lithium will reduce the vapour pressure of liquid ammonia to about 1 at. at 70°C. but the vapour pressure is very sensitive to composition.   Unfortunately, solutions of the alkali metals in ammonia are much less dense than liquid ammonia, thus Li + NH_3 has a density of 0.477 at 19°C. and there is also a positive heat of solution (about 8 k. cals/ml) which would lead to a lower performance.   A summary of the properties of Li solutions in liquid NH_3 is given in Appendix III.   Certain amines are slightly soluble also in liq. ammonia but the addition of carbon containing compounds will render the fuel useless for the fluorine group of oxidants and will rob it of its most important advantage i.e. a low combustion temperature.

This group of fuels has two further important properties. They are very reactive and thus will form self-igniting com-binations with HNO_3 (ammonia requires the addition of about 5% N_2H_4(10)).   It is also to be expected that their combustion efficiency would be high, permitting the use of motors with a small L*.   As they contain no carbon, the exhaust gases from the combustion chamber would give no smoke and, probably, no radar attenuation.

Hydrazine as a Monopropellant and Gas Producer.

Anhydrous hydrazine is an endothermic compound and can therefore be used as a monopropellant.   The Specific Impulse, when the decomposition is to N_2 + H_2, is 167 at a combustion pressure of Pc = 20 ats.   American experience has shown that decomposition to NH_3 by the equation

$$3 \ N_2H_4 \longrightarrow 4 \ NH_3 + N_2$$
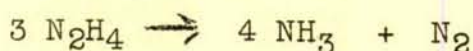
can occur in a rocket motor.   In this case the Specific Impulse is slightly higher.   Decomposition can be initiated by hot wire and certain catalysts have been developed (10).

The disadvantage of anhydrous hydrazine as a monopropellant is its high melting point and there is not sufficient data to determine how much water can be added to the system and still give a reasonable performance.   It should be possible to lower the melting point by the addition of small quantities of other compounds, e.g. some of the metallic compound hydrides might be used or even hydrazine nitrate, which would probably lead to a higher specific impulse.

/5.

- 7 -

5. GENERAL PHYSICAL AND CHEMICAL PROPERTIES.

Ammonia is a colourless gas with a pungent odour, of density 0.65 times that of air; it condenses at -33.4°C., under atmospheric pressure, to a colourless liquid. The vapour pressure of the liquid is 4.2 atmospheres at 0°C., 8.5 atmospheres at 20°C, and 25.8 atmospheres at 60°C (140°F); its density is 0.61 grams per cc at 20°C. Ammonia is very soluble in water, giving an alkaline solution.

Hydrazine is a colourless liquid freezing at + 2°C and boiling at 113.5°C. under atmospheric pressure; its density is 1.01 grams per cc. at 20°C. It has a slight odour, fumes in air, is hygroscopic, and completely miscible with water. In aqueous solution it behaves as a base, rather weaker than ammonia. It forms two sets of salts of the type N_2H_4.H X and N_2H_4.2 HX respectively, but the latter are almost completely hydrolysed in water. It is a very powerful reducing agent, being capable, under some conditions, of reducing salts of silver, gold, copper and mercury to the metals; it reacts violently with some metallic oxides, as described in Section 7 (ii). It interacts with numerous organic compounds (aldehydes, ketones, nitro-compounds, etc.).

Though the name "hydrazine hydrate" is given to an equimolar mixture of hydrazine and water (64.0 per cent N_2H_4 by weight), it is not certain whether, in the liquid state, a true compound N_2H_4.H_2O exists. If it does so, it must be to some extent dissociated, since the constant-boiling mixture at atmospheric pressure is not of exactly equimolar concentration; according to Lobry de Bruyn and Dito (11), it contains 58.5 moles per cent. N_2H_4. The cryoscopic diagram shows, however, that the compound N_2H_4.H_2O exists in the solid state. In the vapour state, though there is some conflict in the published data, it is probable that there is no association between hydrazine and water.

The equimolar mixture, "hydrazine hydrate", melts at -51.5°C, and boils at about 120°C. under atmospheric pressure. There is a eutectic on the water rich side at approximately 40.5 per cent N_2H_4 by weight, -88°C. freezing point, and another on the hydrazine rich side at 69 per cent N_2H_4, freezing at -53.5°C. A mixture containing 73 per cent N_2H_4 freezes at -40°C. Hydrazine solutions show a tendency to supercool. The density of the equimolar mixture is 1.05 at 15°C. It is a colourless, fuming, hygroscopic liquid, with a faint smell like that of hydrazine.

Hydrazine and ammonia form no compound; there is a eutectic mixture freezing at -80°C., containing 13 per cent N_2H_4 by weight. A mixture containing 51 per cent N_2H_4 freezes at -40°C.

More information on the physical properties of these compounds is given in the Appendices.

/6.

6.   <u>CHEMICAL STABILITY.</u>

        Ammonia is a stable chemical compound. Hydrazine on the
other hand, is thermodynamically unstable, and its decomposition
is exothermic.   Its rate of decomposition is, however, so small
under suitable conditions that storage, even in tropical climates,
may prove not to present a serious problem.   The stability on
storage would certainly be much better than that of H.T.P.
Some experimental data pointing to this conclusion may be briefly
reviewed.

        (a) Welsh and Broderson (12) stored 50 ml. samples of 99.7
per cent N_2H_4 in sealed glass vessels at ordinary temperatures,
for up to two years, without observing appreciable decomposition.

        (b) Liquid hydrazine has been heated, in academic laboratory
research, to above 350°C under pressure, and a critical temper-
ature of 380°C has been estimated, without any mishap (13).

        (c) Workers at California Institute of Technology heated
15 ml. of 95.5 per cent N_2H_4 in a 22 ml. bomb.   They found a
rate of rise off pressure at 320°F (160°C) of 2.5 lb. per square
inch per minute, which corresponds to one per cent decomposition in
3 to 5 hours, depending on the gaseous products.   The reaction
appeared to be a surface catalysed vapour phase decomposition (7).

        (d) 90-93 per cent hydrazine has been employed, in the Jet
Propulsion Laboratory, California Institute of Technology, as a
coolant for a section of a rocket motor (c.f. Section ♠).   In
one experiment, the liquid reached 470°F (243°C).   It was of
course only in the chamber for a short time; on the other hand,
it was in contact with copper, which is said to have some catalytic
action on its decomposition.   In other experiments at J.P.L.
explosions occurred at 150°C.   It seems that this was due to the
presence of iron oxides in the cooling jacket (10).

        (e) The M.W. Kellogg Co.(30) heated hydrazine in a stain-
less steel bomb under a nitrogen pressure of about 600 p.s.i.
At 200°C. the decomposition, over 23 hours, did not exceed 1.5
per cent per hour.   At 255°C., however, one experiment led to
sudden decomposition in 30 minutes and another to violent explosion
in 10 minutes.

        Hydrazine in aqueous solution decomposes catalytically in
contact with certain finely divided metals, such as platinum and
nickel.   In neutral solutions the overall reaction is said to be:-

            $3 N_2H_4 = 4 NH_3 + N_2$;
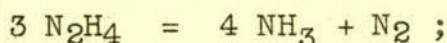
but in presence of excess alkali some hydrogen is produced as
well.   Hydrazine solutions are less stable when excess alkali
is present.   It may be worth while to point out that the solid
catalysts which bring about decomposition of hydrazine are not
always the same as those which decompose hydrogen peroxide.
Silver, for example, is an active catalyst for H_2O_2, but has been
recommended for construction of apparatus in which hydrazine is
distilled.

        Hydrazine solutions are susceptible to oxidation by atmos-
pheric oxygen.   The mechanism is a complex one, hydrogen peroxide
being formed as an intermediate product.   Nearly all the work
done on this reaction has been done on dilute aqueous solutions,
and it is not know how far attack by air could affect concentrated
                                                          /hydrazine

hydrazine or its hydrate, stored in bulk.   (The liquids should however, in any case be stored in closed vessels, as they absorb water and CO_2).   The rate of oxidation, in dilute solution, is greatly increased by excess of alkali, and also by traces of copper.   Audrieth and Mohr (15), in a study of the effect of various substances which form complexes with copper, found that potassium xanthate was a very good inhibitor, and that thiourea, sodium sulphide, cyanide, and thiocyanate and other substances have a considerable effect.   The interesting question suggests itself, whether substances which stabilise hydrogen peroxide against heavy metal ions (e.g. sodium stannate and colloidal tin oxide) will also stabilise hydrazine against either oxidation or catalytic decomposition.   At the moment, however, there is no clear reason for supposing that either hydrazine or its hydrate will require any added stabilisers for storage.

Hydrazine vapour decomposes in contact with a quartz surface at 250-300°C., and at lower temperatures in contact with catalytic metals such as platinum.   The vapour of "hydrazine hydrate" has also been observed to decompose, under some conditions, in contact with hot steel turnings (see Section 8(i)).   This may, however, have been due to the presence of iron oxides on the steel turnings.

7.   COMPATIBILITY.

Hydrazine hydrate can be stored, under temperate climatic conditions, in containers of aluminium, stainless steel, or iron lined with a suitable plastic (oppanol, a polyisobutylene, was used in Germany).   Mild steel leads to discoloration of the hydrate, and might lead to catalytic decomposition in time, though this is not marked at first.   Hot hydrazine hydrate vapour attacks aluminium and its alloys to some extent, so that stainless steel will probably be the best metal for tropical storage vessels (2).   Hot hydrazine hydrate slowly attacks glass, but the cold liquid can be kept in clean glass bottles.

Hydrazine hydrate brought to Britain from Germany (65 tons in March 1947, 11 tons in March 1948), and stored in horizontal stainless steel vessels, is still in good condition in June 1949; thus the 65 ton sample when analysed in March 1947 was 89.9% Hydrazine Hydrate and 89.6% in February 1949;   the 11 ton batch was 85.5% Hydrazine Hydrate in March 1948 and 85.4% in February 1949.

No full study has been made of the compatibility of hydrazine hydrate with plastics.   As indicated above, at least some grades of polyisobutylene may be used.   Rubber is attacked. Sulphur is dissolved chemically so that compositions containing it would not be safe.   Cork is also attacked.

Little can be said at the moment about suitable storage vessels for anhydrous hydrazine, or its mixtures with ammonia, or for ternary mixtures of hydrazine, water and ammonia. The hydrazine-water mixture which freezes at -40°C., which may prove most suitable for Service use, will probably behave very much as does hydrazine hydrate; but experimental confirmation of this will have to be obtained.   The Kellogg Co. (New Jersey) recommend standard stainless steels for storage of anhydrous hydrazine, and state that most plastics and synthetic rubbers can be used with it (30).

/8.Hazards.

8.   <u>HAZARDS</u>.

   i) <u>Explosion Risks</u>.

      Ammonia presents no problem, apart from the possibility
of pressure bursts in faulty containers.   The vapour pressure
of anhydrous NH_3 reaches 26 atmospheres at 60°C. (140°F).

<u>Hydrazine Hydrate</u>.

      This substance does not appear to be detonable in the
liquid state (16).   The vapour, which is probably fully dis-
sociated into N_2H_4 and H_2O (17), will explode when mixed with
air in a proportion of 25 per cent. or more N_2H_6O, according
to German information (2).   Any apparatus or plant in which
hydrazine hydrate above 50 per cent concentration is distilled,
even at low pressure, should be filled with nitrogen.

      The hot vapour of hydrazine hydrate, even in absence of
air, may explode if a catalytic surface is present.   At
Gersthofen, the final fractionating column, in which the hydrate
was concentrated from 50 to 80-90 per cent N_2H_6O, was at one
time packed with cleaned turnings of austenitic stainless steel
(V.2.A).   A mild explosion occurred, however, which damaged
the column, in spite of the fact that it had been filled with
nitrogen.   Laboratory tests were made, in which hydrazine
hydrate vapour was passed over steel turnings, and it was found
that occasional isolated spots glowed red-hot, causing decom-
position of the vapour to N_2, NH_3, and possibly H_2.   After this
observation, the top half only of the final column was packed
with turnings;   the bottom half, which was in contact with the
more concentrated vapour, was fitted with bell-plates of stain-
less steel, in order to avoid exposing a large surface or any
sharp points or corners.   No further explosions occurred during
a few months' running, but whether the danger should be regarded
as entirely eliminated is perhaps open to question (2).   It has
been recently reported that the Western Cartridge Co.(U.S.) has
had an explosion in a distillation column while concentrating
hydrazine hydrate.

<u>Hydrazine</u>.

      An examination has been made of a sample of 92 per cent
material (i.e. 92 per cent N_2H_4, 8 per cent H_2O), in the Sensit-
ivity Section of E.R.D.E.   It was found that there was practically
no sensitiveness to impact or friction, and the lead block
power was very low.   It may be added that a good deal of
academic research on anhydrous hydrazine is reported in the
literature, including experiments in which the substance was
heated to 350°C. or above;   and no specially explosive tendency
has been reported.

      The Bureau of Mines (U.S.A.) have been able to find no
evidence of propagation of detonation in 98% N_2H_4 in steel tubes
of 7/8" diameter, but measurements on the ballistic mortar have
given powers of 135 (T.N.T. = 100).   No such effects were
observed with 85% $N_2H_4.H_2O$.   Sensitivity to impact and to friction
was zero both for 98% N_2H_4 and 85% $N_2H_4.H_2O$ (16).   Confirmatory
evidence is available from M.W. Kellogg Co.(30).

      It seems probable that the vapour of hydrazine may explode
if locally overheated or brought into contact with hot catalytic
surfaces.   In addition, the vapour would of course explode if
mixed with air and ignited.   The vapour of both the hydrate and

                                                    /anhydrous

                           - 11 -

anhydrous hydrazine can be ignited by a spark at a pressure
of 200 mm.. (16).   Metallic sodium dissolves in anhydrous
hydrazine to give a solution in which, by a slow chemical
reaction, a sodium derivative said to be sodium hydrazide,
$NaHN.NH_2$, is formed.   This substance is exceedingly sensitive
to detonation by shock.   The same product is formed when
sodamide reacts with hydrazine (18), and for this reason soda-
mide cannot be recommended as a dehydrating agent for hydrazine
hydrate.   It is less likely that the material would be formed
from caustic alkalis and hydrazine, especially if the hydrazine
was not completely dehydrated, but in any case hydrazine is
said to be particularly unstable in presence of alkalis, so
that the safety of the usual processes for dehydrating the hydrate
requires investigation.

It must also be borne in mind that the oxidation of hydra-
zine under some conditions leads to the formation of hydrazoic
acid or azides.   Hence, any solid deposits, or sludges, observed
in vessels in which hydrazine or its solutions have been in
contact with metals, should be handled with caution.

(ii) Fire Risk.

Ammonia gives rise to no fire risk in air, although it will
burn in oxygen.   Liquid hydrazine hydrate does not ignite in
air, though the vapour, as already mentioned, may explode in air
under some conditions (2).   At ambient temperatures the vapour
pressure of hydrazine hydrate is not sufficient for this to occur.

Anhydrous hydrazine, however, is very inflammable.   It has
also been observed in E.R.D.E. that it will ignite spontaneously
if dropped on to a number of oxides.   Immediate or almost
immediate ignition occurred when a single drop of hydrazine (92
per cent) fell on to cupric oxide, manganese dioxide, silver
oxide, or mercuric oxide;   there was a slightly delayed ignition
with ferric oxide.   On the other hand the oxides PbO, ZnO, MgO,
Al_2O_3, CaO, and BaO seemed to have no action.   In some cases,
with the oxides which caused ignition, two stages could be
distinctly seen: first the oxide in contact with the hydrazine
glowed red-hot (presumably owing to its rapid reduction):   then
the excess hydrazine ignited in the air.   This clearly indicates
a possible danger that if hydrazine, even in absence of air,
comes in contact with small quantities of such oxides, a "hot spot"
may develop from which an exothermic decomposition may spread.
Similar results with ferric oxide have been observed by the
Bureau of Mines (16).

Thin films of anhydrous hydrazine, exposed to the air (e.g.
on rags) may ignite spontaneously after a delay, especially if
exposed to sunlight (30).

The U.S. Bureau of Mines (16) give the minimum concentration
of hydrazine vapour which will ignite in air as 4.67 per cent.
(There is no upper limit, because pure hydrazine vapour will
propagate a flame).   In nitrogen, the lower limit is given as
38 per cent N_2H_4.

(iii) Toxicity.

Ammonia.

The hazard from this substance is well known.   It has a very
pungent smell, and irritates the upper respiratory tract and the

- 12 -
/eyes

eyes.   Owing to the strength of the smell, the presence of
ammonia in the air can be detected at concentrations too low to
be dangerous; the chief risk is that of sudden bursts, leaks,
or spillages which cause an immediate high concentration
locally.   Under such circumstances, workers may be overcome;
or secondary accidents may occur as temporarily blinded persons
try to escape from the locality.   Delayed death from oedema
of the lungs, or bronchitis or pneumonia may follow.   Other
symptoms which have been observed are restlessness, vertigo,
gastric pain, nausea, and disturbance of the bladder function.
Contact of ammonia with the cornea of the eye may lead to
serious or permanent damage (19).   Gas masks containing acti-
vated carbon impregnated with copper sulphate give protection
from ammonia.

        The following table, taken from Jacobs' <u>Analytical Chemistry</u>
<u>of Industrial Poisons, Hazards and Solvents</u>, gives an indication
of the concentrations of ammonia gas in air which give rise to
various degrees of danger.

Maximum concentration tolerable for several hours without serious disturbance.	0.01 per cent by volume.
Concentration dangerous in 30-60 minutes.	0.25-0.45 " " "
Concentration lethal in a few minutes.	0.5 -1.0 " " "
Minimum concentration detectable by odour.	0.0053 " " "

        These figures should not, perhaps, be accepted as established
beyond all doubt.   The authors of a very recent paper (20)
conclude that "the present accepted limit of 100 p.p.m. is
probably safe but needs re-examination."

        It may be added that as ammonia is lighter than air it is
very non-persistent.

        Men working in a high concentration of the gas, protected
by masks, may experience some soreness of the skin in moist areas
(e.g. groin or armpits).   This is probably due to the alkalinity
of ammonia solution.

    <u>Hydrazine and Hydrazine Hydrate</u>.

        Since hydrazine immediately forms its hydrate on contact with
water in the liquid phase, the two may be considered together
for most purposes.   Some further work is needed to give a
complete picture of the poisonous properties of these substances.
The information available at present is summarised below.

        Hydrazine sulphate, administered by subcutaneous injection,
is fatal to mammals in doses of about 0.1 grams per kilogram body
weight.   It has a very specific action on the liver, causing a
kind of "fatty degeneration" of that organ, due to attack on the
parenchymatous cells.   The blood sugar falls; bile pigments and
protein may occur in the urine, but sugar does not.   The recovery
of the liver, with sub-lethal doses, is said to be remarkably
rapid and complete (21).   The actual symptoms observed are first
restlessness and vomiting, then (in fatal cases) depression, fall
in pulse rate, respiratory difficulty, and finally coma and death.
If the blood-sugar content falls very low convulsions may occur

                                                    /before

                            - 13 -

before the end.   The whole process takes a very few days
(22,31).   In non-fatal cases there may be considerable
emaciation.

Izume and Lewis (23) have observed that hydrazine hydrate,
acetate, and sulphate have similar effects upon rabbits in
equivalent amounts, and they conclude that the anion is not
involved.   Bodansky, however, (14) suggests that the free base
is less specific in its action than the sulphate; he found
damage to the kidneys of a dog as well as to the liver.   In one
of Izume and Lewis' experiments, a rabbit was injected with
100 mg. per Kg. hydrazine hydrate; depression was noticed very
soon, and convulsions, followed rapidly by death, took place in
a little under $2\frac{1}{2}$ hours.   The blood sugar content had fallen
from 0.111 to 0.057 per cent.   The Merck Index (5th edition,
U.S.A., 1940) describes the following effects when rabbits were
injected subcutaneously with 0.2 to o.3 g. per Kg. hydrazine
hydrate: "trembling, muscular paralysis, rapid respiration,
clonic spasms, paralysis and death, usually within two hours".
The dose here quoted is much larger than the minimum fatal dose,
which is about 30 mg. of N_2H_4, or 50 mg. of $N_2H_4.H_2O$ per Kg.

                          is required
A fuller study/of the effects of hydrazine vapour, and of
the effects of chronic exposure to vapour, droplets or splashes.
It is not quite clear whether hydrazine, if inhaled, could
react with haemoglobin sufficiently rapidly to act as a blood-
poison.   The evidence available at present regarding the toxic
effects of chronic exposure to hydrazine is a little conflicting,
possibly owing to the differing susceptibility of different
individuals.   (It is likely, inter-alia, that vitamin C
deficiency will cause increased susceptibility).   The fact that
hydrazine and its hydrate have only a slight smell tends to
enhance the danger, though this is to some extent offset by the
fact that both liquids fume visibly in air.   The available
data may be briefly summarised:

(i)   Effect on the Eyes.

According to the chemist in charge of the Gersthofen factory,
some workers who had been exposed to fumes or droplets of hydrazine
hydrate suffered from an irritation of the eyes which might not
be noticed for as much as ten hours afterwards.   The cornea and
eyelids became inflamed and discharged pus, and temporary blind-
ness for two or three days might occur.   Recovery was said to be
complete in a matter of weeks.

Tests were made at C.D.E.S., Porton, in which 30 per cent
solutions of hydrazine hydrate, in water and methyl alcohol
respectively, were instilled into a rabbit's eye on 14 days out
of 16.   Only a slight superficial inflammation resulted, which
cleared up spontaneously within a few days of the final instill-
ation (24).

(ii)   Skin Irritancy.

Apparently no trouble of this kind was met with at Gersthofen
but at Pennemunde it was noticed that a small proportion of workers
(estimated roughly as 3 in 50) were unusually susceptible and
suffered inflammation.   (These workers had been handling mixtures
containing hydrazine hydrate, ethyl alcohol, and traces of
potassium cuprocyanide).   There was also a tendency for cuts

                                                    /already

- 14 -

already present to become septic (25).   Some workers of
R.A.E., Farnborough, who handled "C-stoff" (mixture of
hydrazine hydrate, methanol, water, and trace of cuprocyanide)
experienced a mild inflammation of the hands and fore-arms
(24).

A series of tests was made by C.D.E.S., Porton, with 30
per cent solutions of hydrazine hydrate in water and methanol.
It was found that repeated application of the liquid to the
skin for a fortnight would produce a mild to moderate inflammation
which afterwards cleared up quickly.   No subject tested was
immune, though some suffered worse inflammation than others.
In the worst cases, there was severe itching, which could be
treated with lotions such as calamine lotion.   There was no true
sensitisation dermatitis.   Previous application of vaseline
or lanoline gave some degree of protection (24).

The M.W. Kellogg Co. (New Jersey), after handling anhydrous
hydrazine for about a year and a half, have reported that no
serious toxic effects were observed.   Persons whose hands had
been wetted with the liquid suffered no ill-effect if it was
immediately washed off.   One man whose face was sprayed with
the liquid developed small white blisters, in spite of immediate
washing; these disappeared after two days with application of
vaseline.   Minor irritation of mucous tissues, and headaches,
were sometimes noticed (30).

   (iii) General Systemic effects.

Workers who have been exposed to vapour, droplets, or un-
noticed splashes on the skin have complained of various symptoms,
including headaches, minor stomach troubles, diarrhoea, restless-
ness, and loss of power of concentration (25,26,30).

From general experience it would seem that the effects of
continued exposure to hydrazine and its hydrate can be avoided
by straightforward precautions, including good ventilation, use
of protective clothing (especially rubber gloves).   The gas
masks used for ammonia will give protection from hydrazine,
though it may be necessary to add a cloth filter to stop droplets.
Extra milk, and extra vitamin C in some form, may be helpful to
workers.   Injections of calcium were prescribed in Germany for
persons showing symptoms of poisoning.

9.   DISCUSSION AND CONCLUSIONS.

Ammonia, by far the most available of the three compounds
under discussion, has the following advantages over a hydrocarbon
fuel;

   a) a lower combustion temperature
   b) a slightly higher performance with liquid oxygen
      (although a slightly lower one with Nitric Acid)
and c) possibly a better combustion efficiency.

The disadvantages are its low density and high vapour pressure.
In attempting to remove these disabilities by the addition of
other compounds to liquid ammonia it is essential that the amount
of additive should be small as otherwise the other advantages
will be removed.   It is therefore unlikely that the density can
be greatly increased in practice.   A mixture of liq.NH_3 and
anhydrous N_2H_4 (Table VIII Appendix II) is also not very useful
owing to the small solubility of NH_3 in N_2H_4 at reasonable pressures.
The vapour pressure of liquid ammonia can be very greatly reduced
by the addition of about 11% Lithium but, apart from the question
of the stability of these solutions, the density is also greatly
reduced.   It therefore seems that, on balance, there is no

                                                      /advantage

                          - 15 -

advantage in using liq.NH₃ as a fuel except possibly in small uncooled motors where the high vapour pressure is not too serious a disadvantage.

Hydrazine Hydrate can meet the climatic storage requirements, has about the same performance as a hydrocarbon, and gives a relatively low combustion temperature for about the same performance as a hydrocarbon. Thus it has the advantages of liquid ammonia without the disadvantages.

The main disadvantage of anhydrous hydrazine is its high melting point, and it may well be possible to overcome this. An addition of 26% H_2O is required to lower the setting point to -40°C., but it is possible that other additives, in smaller quantity, may achieve this temperature. Recently the Aerojet Engineering Corporation have shown (33) that both sodium and lithium borohydride are soluble in hydrazine. The sodium salt is more soluble (20.2% by weight) but only reduces the freezing point to -26°C., whereas 12.4% of the lithium salt reduces the freezing point to -44.5°C. Apart from availability the lithium salt would be preferred because of the low molecular weight of lithium. However, it is also understood that with Boron compounds there is always difficulty because of the deposition of the glassy oxide on the walls of the combustion chamber and venturi. If the Services would consider a higher low temperature limit for special purpose weapons, then Hydrazine with 10-20% water would be a practicable fuel, both on performance and probable ease of manufacture.

The main conclusions are :-

i)   liquid ammonia does not merit further consideration either alone or in combination with hydrazine, except possibly as a cheap fuel for uncooled rockets.

ii) more information on stability, toxicity, storage and stability of the system hydrazine/water with less than 36% water is necessary. In particular methods of reducing the melting point of N_2H_4 with additives other than water should be found, e.g. amines, inorganic amides, complex metallic hydrides, etc. This is of particular importance in view of the possible use of ClF_3 as an oxidant.

10.

BIBLIOGRAPHY.

1) Chemistry and Industry, March 26th, 1949, p.206.
2) C.I.O.S. Report No.XXII-18: "Hydrazine Hydrate and C-stoff Production at Gersthofen".
3) Minutes of Liquid Fuels Committee, M.C.A.B., meeting on Sept. 9th 1948: Communication A.C.9896/ LFC.53.
4) L.F. Audrieth and R.A.Penneman, J.A.C.S. 71, p. 1644 (1949).
5) A.G. Parts, A.R.D. Explosives Reports Nos. 234/45 and 245/45.
6) J.G. Aston, D.F. Menard, and M.G. Mayberry, J.A.C.S. 54, p.1530 (1932).
7) J.W. Parsons, T.L. Thompson and T.F. Dixon: "A Survey of Liquid Propellants", North American Aviation Inc. Report No. N.A.4795.
8) C.R. Forster: "Preliminary Experiments with Hydrazine as a Rocket Motor Coolant", J.P.L. Progress Report No.4-45.
9) A.J. Stosick: "Liquid Propellants for Rockets", J.P.L. Progress Report No.9-9.
10) British Joint Services Mission, Washington: Explosives and Propellants News Letter No.S.M.2. (Feb.1949).
11) J.W. Mellor, Comprehensive Treatise, Vol.VIII., p.311.
12) T.W.B. Welsh and H.J. Broderson, J.A.C.S. 37, p.816 (1915).
13) International Critical Tables, ed.I., vol.3. pp.228-9.
14) M. Bodansky, J. Biol. Chem. 58, p.799 (1924).
15) L.F. Audrieth, B.J. Ackerson, et alia; "The Chemistry of Hydrazine", University of Illinois, 1948 (N.6.ori-71-Chemistry Task No.XX).
16) "Explosive Properties of Hydrazine", U.S. Bureau of Mines, May 1949.
17) P.A. Giguere and R.E. Rundle, J.A.C.S. 63, p.1135 (1941).
18) R. Stolle, J. Prakt Chem.83, p.200.
19) A.J. Lanza and J.A. Goldberg, Industrial Hygiene (Oxford Medical Publications, 1939), p.503.
20) L. Silverman, J.L. Whittenberger, and J. Muller, (Journ. Industrial Hygiene and Toxicology, March 1949, p.74).
21) H.G. Wells, Journal Exp. Med. X. p.457 (1908).
22) F.P. Underhill et alia, J. Biol. Chem. 4y p.165 (1908); ibid 10, p.159 (1911); 22 p.499 (1915); 27, p.169 (1916); 58, p.147 (1924). Compare also B.M. Hendrix and A.J. McAmis, ibid, 61 p.45 (1924); Lewis and Izume, ibid 71, p.33 (1926); Curti, Riv. Pat. Nerv.42, p.27 (1933); J.Conn, J.Amer.Med.Assoc. 134, p.130 (1947).
23) S. Izume and B. Lewis, J. Pharm. & Exp. Therapeutics, XXX, p.87 (1927).
24) B. Woolcott and T.W.N. Truckle, C.D.E.S. Porton Technical Paper No.22 (Sept.1947).
25) T.E.E. Greenock, S.T.R. No.487 (Dec.1945): "The Broad Features of the German Development of Hydrogen Peroxide as a Propulsive", p.31.
26) Lewin, Gifte unde Vergiftung, under heading "Hydrazine".

27) "The Storage and Handling of Hydrazine
Hydrate" (Instructions issued by S.E.I.,
A.R.D. Woolwich, October 18th 1946.)

28) F.I.A.T. Final Report No.839: "Production
of Hydrazine Hydrate", by J. Robell.

29) News Letter END/2/48, by E.N. Dodd.

30) M.W. Kellogg Co., Special Projects Dept.,
Jersey City, New Jersey, Report No. SPD.134
(March 19th, 1948).

31) S. Minami, Jap. J. Exp. M.11, pp.253 & 475
(1933).

32) D.W. Scott et alia, J.A.C.S. 71, p.2293 (1949).

33) D.L. Armstrong & J.F. Warfel. Investigation of
Liquid Rocket Propellants. Aerojets Engineering
Corporation Report No.820-4.

34) H. Maisner & F. Zwicky. Light Metal Amides
and Compounds of a Similar Nature. Aerojet
Engineering Corporation Report No.RTM-30.

35) M.I.T., Hydrogen Peroxide Laboratories, NOrd 9107,
Task C, Progress Report No.21 (30.4.47) pp.5-6.

Performance of NH_3, $N_2H_4.H_2O$ and N_2H_4 with various oxidants

TABLE I

Performance of oxidant, 100% HNO_3 with various fuels at Pc = 20 ats.

(a) Fuel = n-Decane.

Wt. Ratio	Tc(^{O}K)	γ	S.I. (secs.)	S.I. x $\bar{\delta}$
2.56	2000	1.283	198.4	231
3.04	2400	1.255	210.6	252
3.70	2800	1.230	219.3	271
4.12	2950	1.221	221.2	278
6.25	2950	1.210	210.3	278
7.44	2800	1.211	202.2	272
9.94	2400	1.223	184.2	255
12.69	2000	1.241	166.4	234

(b) Fuel = $N_2H_4.H_2O$

Wt. Ratio	Tc(^{O}K)	γ	S.I.	S.I. x $\bar{\delta}$
.6804	2000	1.2538	202.9	240
.7976	2200	1.2411	209.0	251
.9425	2400	1.2291	213.9	261
1.0811	2400	1.2280	210.9	261
1.386	2200	1.2309	197.7	251
1.7514	2000	1.2470	184.8	240

(c) Fuel = liq. NH_3

Wt. Ratio	Tc(^{O}K)	γ	S.I.	S.I. x $\bar{\delta}$
.1071	2000	1.2632	207.7	195
.1209	2200	1.2496	213.4	206
.1363	2400	1.2373	218.3	216
.2009	2400	1.2324	206.8	223
.2402	2200	1.2410	194.3	218
.2833	2000	1.2505	182.2	211

(d) Fuel = N_2H_4

Wt. Ratio	Tc(^{O}K)	γ	S.I.	S.I. x $\bar{\delta}$
.1285	2000	1.2987	223.2	254
.1961	2400	1.2695	233.1	275
.2910	2800	1.2429	238.6	293
.5125	2800	1.2315	222.1	289
.7619	2400	1.2428	198.2	267
1.0159	2000	1.2588	176.7	244

TABLE II

Performance of oxidant, ClF_3, with various fuels at Pc = 20 ats.

(a) Fuel = N_2H_4

Wt. Ratio		$Tc(^{O}K)$	γ		S. I.		S.I. x $\bar{\delta}$	
i	ii		i	ii	i	ii	i	ii
.4832	.5225	2000	1.3387	1.3386	223.8	221.7	264	264
.7082	.7603	2400	1.3253	1.3252	234.9	233.7	290	290
.9837	1.0711	2800	1.3147	1.3144	243.5	240.2	314	314
1.1697	1.2728	3000	1.3111	1.3107	246.2	242.8	326	325
1.3924	1.5167	3200	1.3086	1.3081	248.3	244.7	337	336
1.6749	1.8356	3400	1.3076	1.3069	249.6	245.7	348	347
2.0205	2.2311	3600	1.3080	1.3071	250.5	246.2	358	357

(i) - $\Delta H_f (ClF_3)$ = 30 k.cals./mol.   (ii) - $\Delta H_f (ClF_3)$ = 42 k.cals./mol.

(b) Fuel = liq. NH_3

Wt. Ratio		$Tc(^{O}K)$	γ		S. I.		S.I. x $\bar{\delta}$	
i	ii		i	ii	i	ii	i	ii
1.4224	1.5383	2000	1.3397	1.3396	208.9	205.8	206	207
1.7351	1.8753	2400	1.3255	1.3253	221.5	218.1	230	232
2.1328	2.3201	2800	1.3139	1.3135	231.2	227.4	254	255
2.3870	2.6076	3000	1.3099	1.3093	235.1	231.0	266	268
2.7044	2.9674	3200	1.3071	1.3065	238.1	233.8	278	280
3.1147	3.4335	3400	1.3060	1.3056	240.3	235.9	291	293

(i) - $\Delta H_f (ClF_3)$ = 30 k.cals./mol.   (ii) - $\Delta H_f(ClF_3)$ = 42 k.cals./mol.

(c) Fuel = $N_2H_4.H_2O$

Wt. Ratio	$Tc(^{O}K)$	γ	S. I.	S.I. x $\bar{\delta}$
.6521	2000	1.3030	204.17	253.0
.8704	2400	1.2901	216.65	278.6
1.1513	2800	1.2813	226.25	302.27
1.3478	3000	1.2793	229.75	313.6
1.4793	3100	1.2796	231	319.5

The calculations on ClF_3 have been carried out: (a) with two possible heats of formation which are the limits of uncertainty in this property, (b) the dissociation of HF has been neglected but this introduces a negligible error and (c) no calculations of system in which free fluorine can be formed, i.e. oxidant rich systems, have been made owing to the great uncertainty of the thermodynamic properties of Fluorine (c.f. E.R.D.E. Tech. Memo. No.6/M/49)

TABLE III

Performance of oxidant, liq.O_2, with various fuels at Pc = 20 ats.

(a) N_2H_4

Wt. Ratio	Tc(^{O}K)	γ	S.I. (secs.)	S.I. x $\bar{\delta}$
.249	1906	1.309	236.5	245
.333	2272	1.286	246.0	256
.399	2576	1.270	252.5	264
.665	3083	1.240	264	279
1.000	3500	1.228	257	276

(b) liq.NH_3

Wt. Ratio	Tc(^{O}K)	γ	S.I. (secs)	S.I. x $\bar{\delta}$
.704	1840	1.283	219	202
.94	2361	1.243	242	229
1.13	2806	1.200	251.6	242

(c) Aviation Gasoline (Density 0.720 gm./cc. at 10°C)

Wt. Ratio	Tc(^{O}K)	γ	S.I. (secs.)	S.I. x $\bar{\delta}$
1.5	1817	1.285	200.4	190
2.0	2861	1.235	235.7	226
3.0	3383	1.212	237.8	237
3.5	3406	1.211	233.9	236

Physical Properties of Ammonia, Hydrazine Hydrate & Anhydrous Hydrazine

TABLE IV

Comparison of Most Important Physical Properties

Property	NH_3	$N_2H_4.H_2O$	N_2H_4
Boiling Point ($^\circ$C.)	-33.5	118.5/740 mm.Hg.	113 to 113.5
Melting Point ($^\circ$C.)	-77.7	-51.5	+2 to +1.4
Density (gr./cc.)	0.616/16.5°C.	1.0305/21°C.	1.013/15°C.
Critical Temp.($^\circ$C.)	132.4	-	380
Critical Pressure (ats.)	111.5	-	145
Heat of Formation (300°K)	-15.84 (liquid) -10.94 (gas)	-58.05	+12.05

TABLE V

Physical Properties of Liquid & Gaseous Ammonia

(a) Vapour pressure of liquid ammonia

T$^\circ$C.	-60	-30	0	30	60	80	100	120
P(ats.)	.216	1.179	4.238	11.512	25.797	40.902	61.816	89.802

(b) Density of liquid ammonia

T$^\circ$C	-70	-50	-30	-10	0	+20
Density (gr./cc.)	0.725	.705	.677	.652	.638	.610

TABLE VI
Physical Properties of Anhydrous Hydrazine

(a) Vapour pressure

T$^\circ$C	0	20	.40	60	140	170	200	300	380
P (ats.)	.0035	.0139	.0445	.122	2.27	5.0	10.0	56.3	145

(b) Density

T($^\circ$C)	0	20	50
Density (gr./cc.)	1.0253	1.0083	0.9828

These figures are calculated from the equation

$$d = 1.0253 (1- 0.00085\ t) \qquad (t = deg.C.)$$

(c) Specific Heat of Hydrazine

0.75 calories per gram per $^\circ$C   (30)

/Table VII

TABLE VII

Physical Properties of Hydrazine-Water Mixtures

(a) Vapour Pressure of Hydrazine Hydrate (28)

$T^{\circ}C.$	40	60	80	100	119
P (mm.Hg.)	20	55	135	325	760

These figures have been obtained from a curve in Ref. 28.

(b) Density of System-Hydrazine/Water at $15^{\circ}C$ (Ref. 11)

Wt. per cent of N_2H_4	0.0	14.0	26.45	40.85	64.1	80	100
Density (gr./cc.)	0.9991	1.0142	1.0272	1.0389	1.0470	1.0379	1.0114

(c) Freezing Point of System - Hydrazine/Water

Wt. per cent N_2H_4	0	20	40.5(i)	50	60(ii)	64(2i)	69(i)	73	80	90	100
$T^{\circ}C.$	-8	-22	-88	-65	-52.5	-51.5	-53.5	-40	-25	-9	+22

(i) Eutectic   (ii) Hydrazine Hydrate

(d) Composition of Ternery Mixtures containing NaOH (4)

Certain of these mixtures, at temperatures above $60^{\circ}C.$ form a two phase system. No similar effect is found with KOH, K_2CO_3, Na_2CO_3 Na_3PO_4 or Na_2SO_4. The table gives some actually observed compositions.

$T^{\circ}C$	Material	Wt. per cent N_2H_4	NaOH
100	Upper Phase	92.7	2.4
90	"	92.2	2.0
70	"	90.9	3.2
60	"	77.5	9.3
100	Lower Phase	5.7	70.3
90	"	5.9	69.3
70	"	6.7	67.6
60	"	19.0	51.4
100	Plait Point	45.9	27.9
90	"	45.6	28.2
70	"	45.4	28.5
60	"	45.5	29.6

(e) Specific Heat of Hydrazine Hydrate: 0.78 calories per gram per $^{\circ}C.$ (30)

TABLE VIII

Vapour Pressures of Saturated Solutions of N_2H_4 in liquid NH_3
(in equilibrium with solid N_2H_4) (Mellor "Comprehensive
Treatise" VIII p.315)

$T(^{\circ}C.)$	Wt. per cent N_2H_4	p (mm.Hg.)
-80 (eutectic)	13	40
-70	19.5	78
-60	29.1	145
-50	39.7	252
-40	51.0	395
-30	63.8	562
-20	76.0	675
-10	87.6	620
-5	92.6	470
0	98.0	175
+1	98.6	105

The Properties of Solutions of Lithium in Liquid Ammonia

The alkali metals have a high solubility in liquid ammonia but, on account of the importance of the molecular weight of combustion products, only the system with Lithium metal can be considered as a fuel for rocket propulsion. It would suffer from the disadvantage of being highly attenuating. The alkaline earth metals form solutions of the compound $M.(NH_3)_6$, except Mg. which is insoluble. Aluminium is also insoluble and this fact, in conjunction with the insolubility of Mg. makes it almost certain that Be would be insoluble. The only practicable system, NH_3 + metal, is therefore Lithium + NH_3. Johnson and Piskur (J.Phys.Chem. XXXVII p.93 (1933)) give the following figures for the vapour pressure of NH_3 over saturated solutions of Li in liq. NH_3.

$T^{\circ}C.$	Vapour Pressure (mm.Hg.)	mols.NH_3/Li	Wt. % Li
0	34.0	3.60	11.32
-32.7	3.4	3.74	10.90
-33.2	3.4	3.75	10.89
-63.5	1.1	3.81	10.70

From this it can be seen that the solubility of Li in liquid ammonia is only slightly dependent on the temperature and that the Li reduces the vapour pressure of liquid ammonia by a factor of about 20.

Ruff & Zedner (Berichte 41 p. 1948 (1908)) give the following figures for the boiling points and setting points of solutions of Li in liquid NH_3.

Atom per cent Li	Boiling Point	Atom per cent Li	Setting Point
2.31	-33.1	0	-76
3.17	-33.0	6.8	-77
5.74	-32.7	9.9	-77.5
8.72	-31.7	15.6	-79
11.28	-29.8	22.9	No solidification down to temp. of liquid air
11.83	-29.5		
16.04	-19.4		
25.5 (saturated)	+63		
(11.7% by.wt.)			

Jaffe (Zeit. f. Physic 93 p.741 (1935)) showed that the setting point of the saturated solution was $-181^{\circ} \pm 3^{\circ}C.$

The heat of solution of Li in liquid ammonia is slightly exothermic, Kraus and Schmidt (J.A.C.S. 56 p. 2297 (1934)) stating a value of 8.0 kilocalories per mol.

Thus, as far as vapour pressure and solubility are concerned, solutions of Li in liq. NH_3 are very attractive as fuels. The slight loss of energy in forming the solution is not important and in any case would be more than compensated by heat of formation of Li_2O formed during the combustion of the fuel. However, there are two disadvantages. The first, that of chemical instability, may or may not be insuperable. The various authors referred to mention the necessity for pumping off hydrogen which is formed on solution but give no information as to whether hydrogen is evolved subsequently. Schechter, Thomson & Kleinberg (J.A.C.S. 71 (1949) p.1816)

/give

give experimental data on the oxidation of Na in liq.NH₃ to the amide or the oxide, depending on the experimental conditions by gaseous oxygen. Similar oxidation may also occur with Li. solutions. This is not an insurmountable difficulty but does add to the handling problems.

Finally it should be mentioned that the Aerojet Engineering Corporation (33) have found that in solutions of Li in liq.NH₃ the metal amide is formed quite fast at 0°C. and observably at -78.5°C.

An even more serious objection is the extremely low density of solutions in liquid ammonia. Jaffe (loc.cit.) gives the following figures for the density of the saturated solution:-

at $+19^{\circ}$C. $d = 0.477 \pm 0.006$ gr./cc.
at -80°C. $d = 0.495 \pm 0.006$ "   "

The density is thus much lower than that of liquid NH₃ (0.610 gr./cc at 20°C.) which virtually rules out the use of this fuel for the majority of weapons.

It might be possible to reduce the vapour pressure by the addition of salts such as LiAlH₄. This salt reacts, according to information quoted in "Preliminary Data Sheet No.4 (dated 1.5.49) of "Metal Hydrides Incorporated", as follows:-

$$2 \text{ LiAlH}_4 + 5\text{NH}_3 \longrightarrow (\text{LiAlH(NH}_2)_2)_2 \text{ NH} + 6\text{H}_2$$
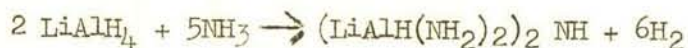
If the product is stable and only small quantities are required it might be worth while doing a little work on this system and possibly with LiAlH₄ or a similar salt in anhydrous Hydrazine.

It is shown in Ref. 33 that both Lithium and Sodium Borohydride are soluble in liquid ammonia. The minimum freezing point with the first salt is $+8^{\circ}$C. but a 50% solution of the sodium salt has a freezing point -26°C. and a vapour pressure of about 1 at. The density of this solution is believed to be between 0.7 - 0.8 gr./cc. and its cost per lb. would probably be higher than that of anhydrous hydrazine. It, therefore, seems more reasonable to concentrate on hydrazine where difficulties due to the deposition of oxide (i.e. B₂O₃) do not occur. It should also be stressed that the stability of the solutions of these borohydrides in NH₃ and N₂H₄ does not seem to have been investigated. A summary of the properties of amides and similar compounds and the properties of solution of metals and salts in liquid ammonia is given in Ref. 34.
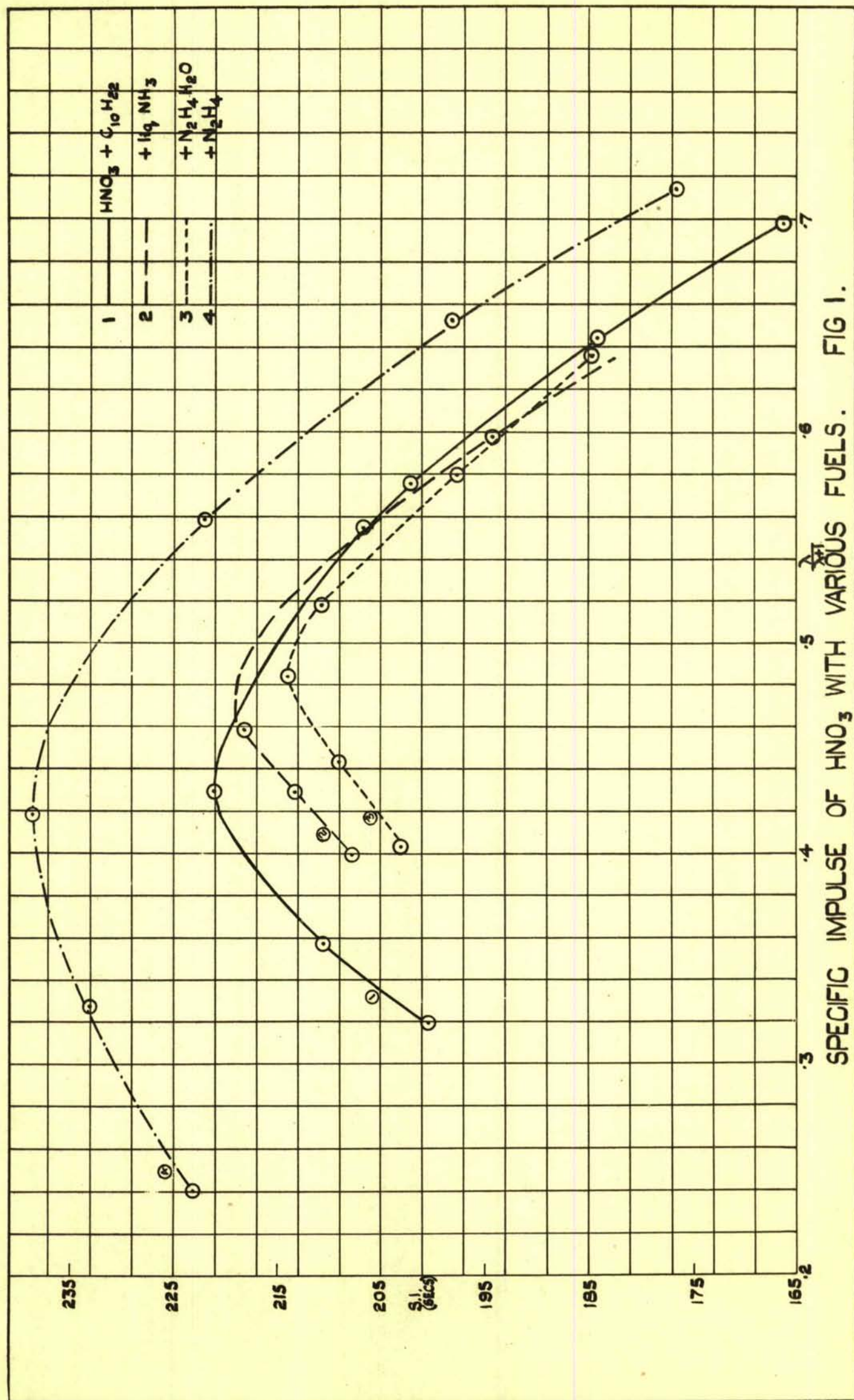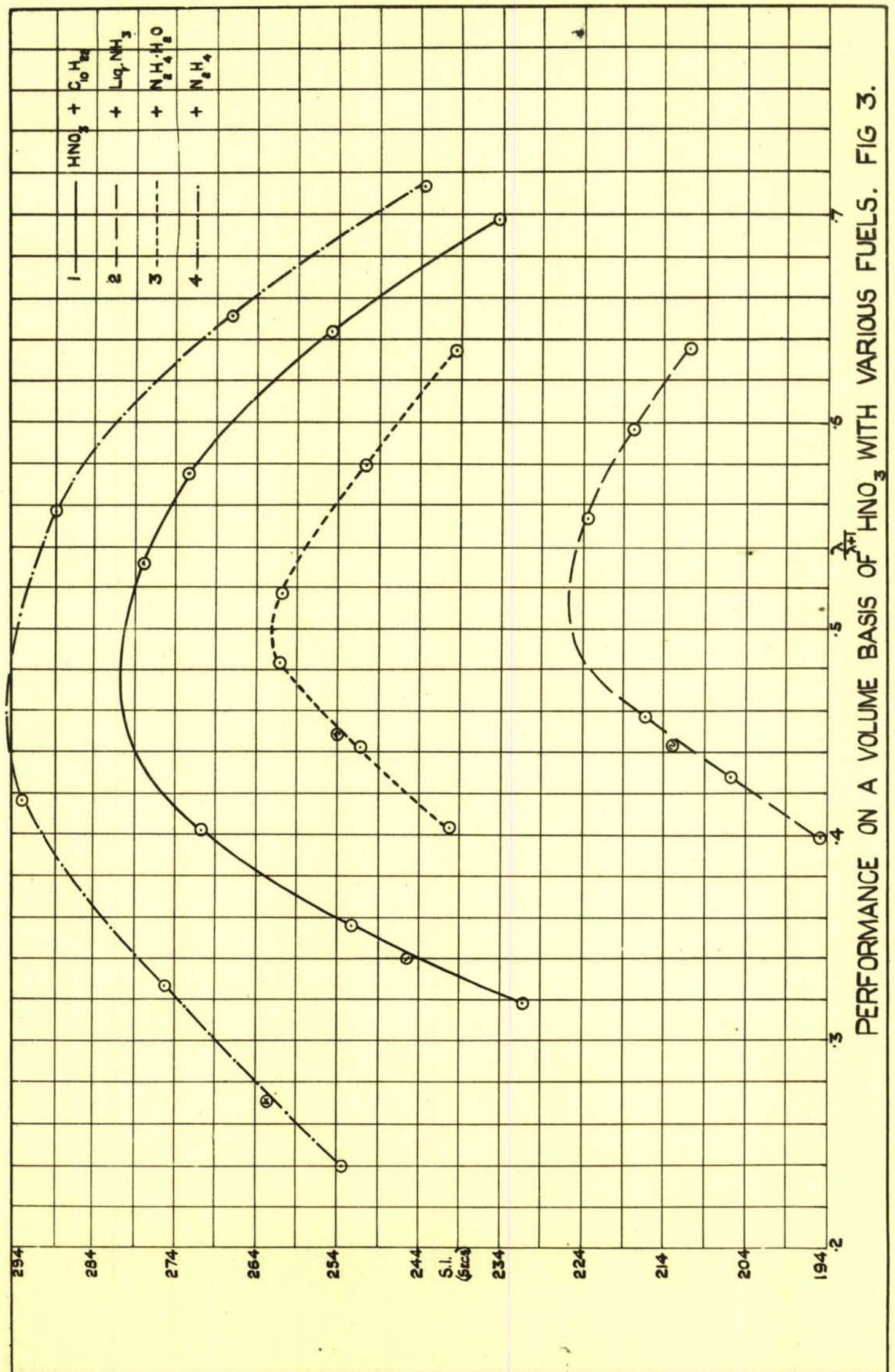
S. No. 100
M.No.405/49

ACKNOWLEDGMENTS.

SPECIFIC IMPULSE OF HNO₃ WITH VARIOUS FUELS. FIG 1.

A COMPARISON OF CIF_3 WITH HNO_3 ON A WEIGHT BASIS. FIG 2.

1	N_2H_4	$+ CIF_3$
2		$+ HNO_3$
3	NH_3	$+ CIF_3$
4		$+ HNO_3$
5	$N_2H_4 \cdot H_2O$	$+ CIF_3$
6		$+ HNO_3$

PERFORMANCE ON A VOLUME BASIS OF HNO$_3$ WITH VARIOUS FUELS. FIG 3.
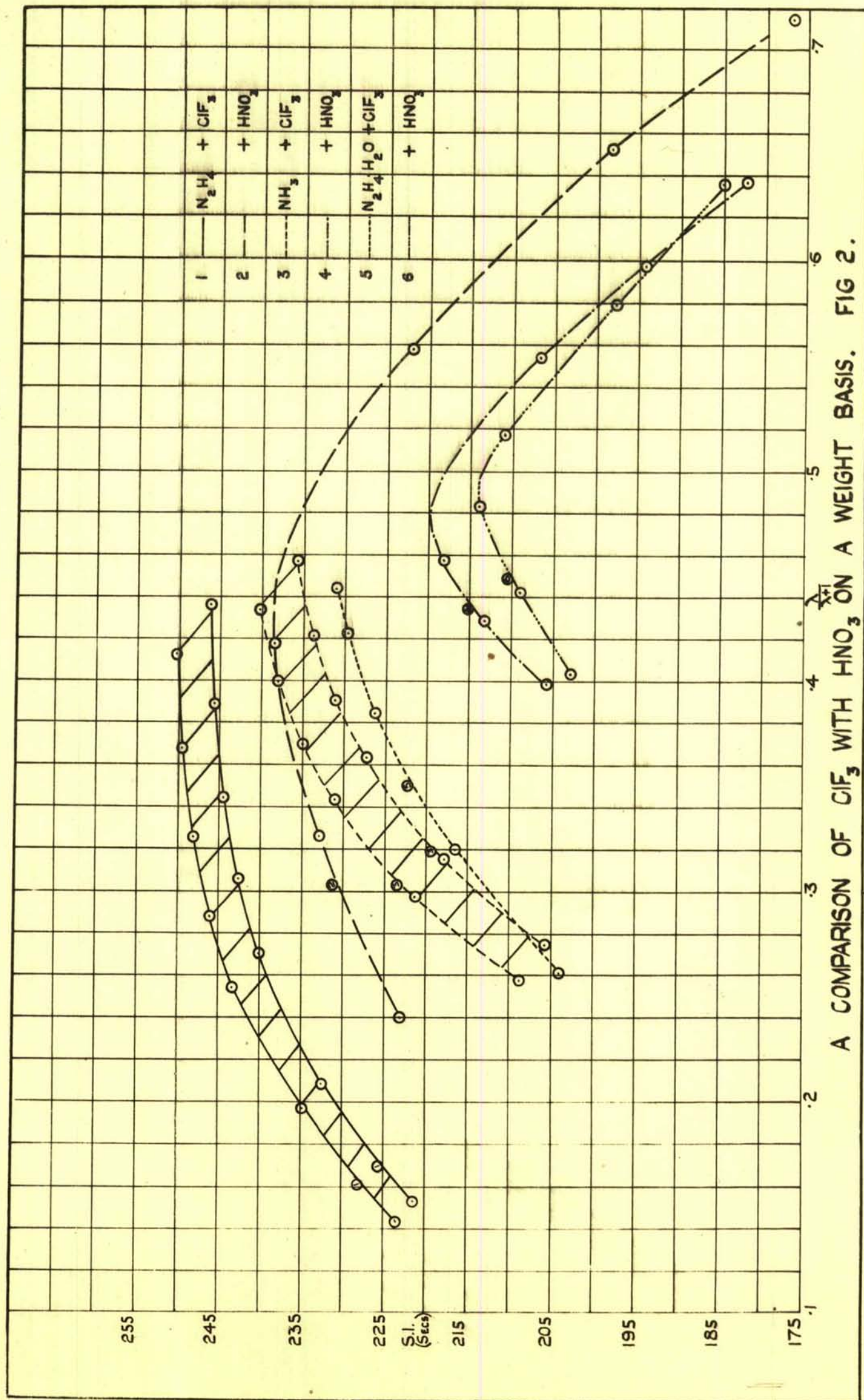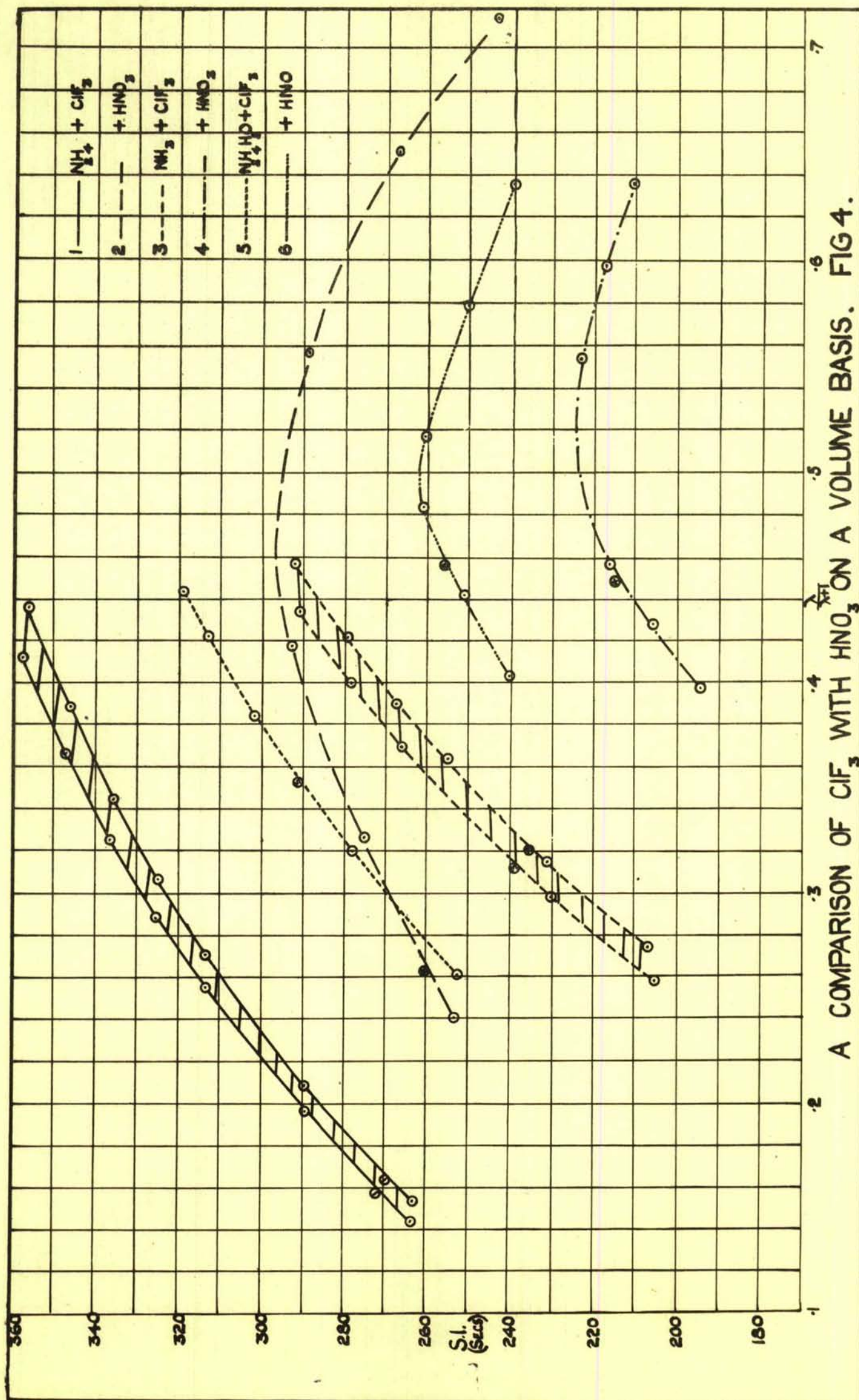
A COMPARISON OF ClF$_3$ WITH HNO$_3$ ON A VOLUME BASIS.   FIG 4.